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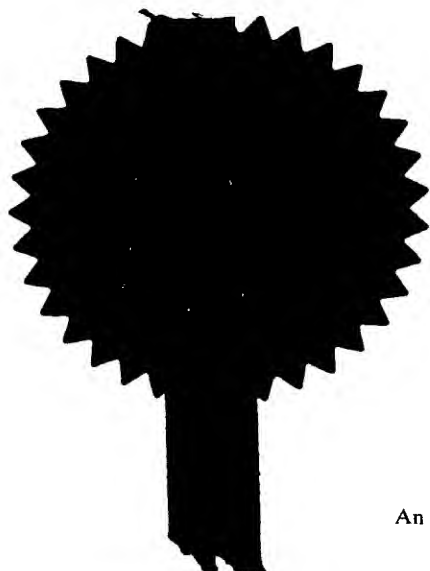
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Signed *Andrew Genge*  
Dated 10 March 2000



# Patents Form 1/77

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## Request for grant of a patent

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1. Your reference SMC 60341

2. Patent application number  
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3. Full name, address and postcode of the or of each applicant (underline all surnames)  
Zeneca Limited  
15 Stanhope Gate  
London  
W1Y 6LN

Patents ADP number (if you know it) 6254007002

If the applicant is a corporate body, give the country/state of its incorporation United Kingdom

4. Title of the invention COMPOSITIONS

5. Name of your agent (if you have one)  
"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)  
MAYALL, John  
Zeneca Specialties  
Hexagon House  
P O Box 42  
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Manchester M9 8ZS

Patents ADP number (if you know it) 6244313002X 15081001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country	Priority application number (if you know it)	Date of filing (day / month / year)
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7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing (day / month / year)
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8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:  
a) any applicant named in part 3 is not an inventor, or  
b) there is an inventor who is not named as an applicant, or  
c) any named applicant is a corporate body.  
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22/2 P. 799 NO.

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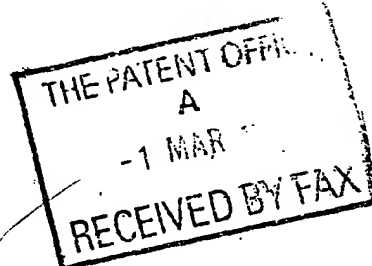
Claim(s)

Abstract

Drawing(s)

21

2



10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11.

I/We request the grant of a patent on the basis of this application.

Signature

*C. Terry*

Date 1 March 1999.

Zeneca Limited Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom

K.M. Pinder/G. Terry 0161.721 1361/2

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Patents Form 1/77

COMPOSITIONS

The invention relates to compositions containing pigments and to their use in inks for ink-jet printing.

Ink jet printing involves printing an image onto a substrate using ink droplets ejected through a fine nozzle onto a substrate without bringing the fine nozzle into contact with the substrate.

There are many demanding performance requirements for colorants and inks used in ink jet printing. For example they desirably provide sharp, non-feathered images having good water-fastness, light-fastness and optical density. The inks are often required to dry quickly when applied to a substrate to prevent smudging, but they should not form a crust which would block the tip of the fine nozzle. The inks should also be stable to storage over time without decomposing or forming a precipitate which could also block the fine nozzle.

Thermal and piezoelectric ink jet printers are widely used, thus there is a need for inks, suitable for use in both types of printers, having high colour strength and giving images having a high light-fastness and water-fastness when printed on a typical substrate, especially plain paper.

It has now been found that the combination of a pigment with a low molecular weight hydrophilic polymer and a high molecular weight hydrophobic polymer in a liquid medium results in a composition which is suitable as an ink for use in thermal and piezo ink-jet printers.

Thus, according to the present invention there is provided a composition comprising the components:

- (a) a hydrophilic polymer having a number average molecular weight less than 30,000;
- (b) a hydrophobic polymer having a number average molecular weight more than 40,000;
- (c) pigment; and
- (d) liquid medium.

The number average molecular weight ( $M_n$ ) for the components (a) and (b) may be measured by any of the well known techniques, preferably by gel permeation chromatography ("gpc"). The gpc method used for determining  $M_n$  preferably comprises applying the polymer to a chromatography column packed with cross-linked polystyrene/divinyl benzene, eluting the column with tetrahydrofuran at a temperature of 40°C and assessing the  $M_n$  of the polymer compared to a number of a polystyrene standards of a known  $M_n$ . Suitable cross-linked polystyrene/divinyl benzene chromatography columns are commercially available from Polymer Laboratories.

As an alternative to the gpc method for determining Mn one may use other methods, for example multi-angle light scattering.

Preferably the Mn of component (a) is less than 20,000, more preferably less than 12,500 and especially less than 10,000. Preferably the Mn of component (a) is greater than 500. Preferably the Mn of component (b) is greater than 60,000. Preferably the Mn of component (b) is less than 10 million, more preferably less than 2 million.

Component (a) is preferably hydrophilic by virtue of the presence of ionic and/or nonionic water dispersing groups in the hydrophilic polymer. The hydrophilic polymer is preferably prepared by polymerising one or more monomers having water-dispersing groups, optionally with one or more monomers which are free from water-dispersing groups. The nature and level of water-dispersing groups in the polymer influences whether a solution, dispersion, emulsion or suspension is formed on dissipation of the hydrophilic polymer in aqueous media. Preferably the level of monomers having water-dispersing groups is from 5 to 80% by weight of the hydrophilic polymer. Preferably a solution is formed on dissipation of the hydrophilic polymer, although minor amount of the hydrophilic polymer may be insoluble in water and exist as dissipated particles when mixed with aqueous media or water.

Water-dispersing groups are preferably pendant to the main polymer backbone. Water-dispersing groups may be ionic and/or non-ionic. Preferred ionic water-dispersing groups are anionic water-dispersing groups, especially carboxylic, phosphonic and or sulphonic acid groups. Preferred non-ionic water-dispersing groups are polyoxyalkylene groups, more preferably polyoxyethylene groups.

The anionic water-dispersing groups are preferably fully or partially in the form of a salt. Conversion to the salt form is optionally effected by neutralisation of the polymer, preferably during the preparation of the hydrophilic polymer and/or during the preparation of the composition of the present invention. If anionic water-dispersing groups are used in combination with a non-ionic water-dispersing group, neutralisation may not be required.

Preferably the base used to neutralise any anionic water-dispersing groups is ammonia, an amine or an inorganic base. Suitable amines include tertiary amines, for example triethylamine or triethanolamine. Suitable inorganic bases include alkaline hydroxides and carbonates, for example lithium hydroxide, sodium hydroxide, or potassium hydroxide. A quaternary ammonium hydroxide, for example  $N^+(CH_3)_4OH^-$ , can also be used. Generally a base is used which gives the required counter ion desired for the composition. For example, preferred counter ions include  $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $NH_4^+$  and substituted ammonium salts.

Component (b) is preferably hydrophobic by virtue of being free from or having low levels of ionic and/or non-ionic water-dispersing groups. The hydrophobic polymer is preferably prepared by polymerising one or more monomers which are free from or having low levels of ionic and/or non-ionic water-dispersing groups. Preferably the level

of monomers having water-dispersing groups is from 0 to 25% by weight of the hydrophobic polymer. Preferably the level of monomers having water-dispersing groups is at least 5% by weight greater in the hydrophilic polymer than the level of monomers having water dispersing groups in the hydrophobic polymer. More preferably the level of monomers having water-dispersing groups is at least 10% by weight greater in the hydrophilic polymer than the level of monomers having water dispersing groups in the hydrophobic polymer. Although the hydrophobic polymer has only a low solubility in pure water, it is preferably chosen such that it does not precipitate out when in the composition of the invention.

The hydrophilic and hydrophobic polymers may each be homopolymers or copolymers.

Component (a) is preferably a hydrophilic acrylic, polyurethane or polyester polymer, especially a hydrophilic acrylic or polyurethane polymer, having a  $M_n$  less than 30,000.

When component (a) is a hydrophilic acrylic polymer it preferably has a glass transition temperature ( $T_g$ ) greater than  $-10^\circ\text{C}$  and more preferably from  $20^\circ\text{C}$  to  $120^\circ\text{C}$ .  $T_g$  is the temperature at which the polymer changes from a glassy, brittle state to a plastic, rubbery state, and may be measured by differential scanning calorimetry.

When component (a) is a hydrophilic acrylic polymer it preferably has an acid value from 30 to 200mgKOH/g, more preferably from 30 to 150mgKOH/g and especially from 40 to 100mgKOH/g.

The hydrophilic acrylic polymer has preferably been obtained from the polymerisation of one or more olefinically unsaturated monomers having ionic and/or non-ionic water-dispersing groups, optionally in the presence of one or more olefinically unsaturated monomers which are free from ionic and non-ionic water-dispersing groups.

Preferred olefinically unsaturated monomers having ionic water-dispersing groups include but are not limited to acrylic acid, methacrylic acid, itaconic acid,  $\beta$ -carboxy ethyl acrylate, maleic acid, monoalkyl itaconates (for example, monomethyl maleate, monoethyl maleate, monobutyl maleate and monooctyl maleate), citraconic acid, styrenesulfonic acid, vinylbenzylsulfonic acid, vinylsulfonic acid, acryloyloxyalkyl sulfonic acids (for example, acryloyloxymethyl sulfonic acid, acryloyloxyethyl sulfonic acid, acryloyloxypropyl sulfonic acid and acryloyloxybutyl sulfonic acid), methacryloyloxymethyl sulfonic acid, methacryloyloxyethyl sulfonic acid, methacryloyloxypropyl sulfonic acid and methacryloyloxybutyl sulfonic acid), 2-acrylamido-2-alkylalkane sulfonic acids (for example, 2-acrylamido-2-methylethanesulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid and 2-acrylamido-2-methylbutane sulfonic acid), 2-methacrylamido-2-alkylalkane sulfonic acids (for example, 2-methacrylamido-2-methylethanesulfonic acid, 2-methacrylamido-2-methylpropanesulfonic acid and 2-methacrylamido-2-methylbutanesulfonic acid), mono-(acryloyloxyalkyl)phosphates (for

example, mono(acryloyloxyethyl)phosphate and mono(3-acryloyloxypropyl)phosphates) and mono(methacryloyloxyalkyl)phosphates (for example, mono(methacryloyloxyethyl)phosphate and mono(3-methacryloyloxypropyl)phosphate).

5 Especially preferred olefinically unsaturated monomers having ionic water-dispersing groups include acrylic acid, methacrylic acid, itaconic acid,  $\beta$ -carboxy ethyl acrylate, and / or maleic acid.

Preferred olefinically unsaturated monomers having non-ionic water-dispersing groups include alkoxy polyethylene glycol (meth)acrylates, preferably having a Mn of from 350 to 2000. Examples of such monomers which are commercially available include  $\omega$ -methoxypolyethylene glycol acrylate.

Preferred olefinically unsaturated monomers which are free from ionic or non-ionic water-dispersing groups include alkyl(meth)acrylates, optionally substituted styrenes, methacrylamides, pyrrolidones, and allyl compounds.

15 Preferred alkyl(meth)acrylates contain less than twenty carbon atoms. Examples include methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, sec-butyl acrylate, amyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, octyl acrylate, tert-octyl acrylate, 2-phenoxyethyl acrylate, 2-chloroethyl acrylate, 2-bromoethyl acrylate, 4-chlorobutyl acrylate, cyanoethyl acrylate, 2-acetoxyethyl acrylate, dimethylaminoethyl acrylate, benzyl acrylate, methoxybenzyl acrylate, 2-chlorocyclohexyl acrylate, acrylate, acetoacetate, cyclohexyl acrylate, furfuryl acrylate, tetrahydrofurfuryl acrylate, phenyl acrylate, 5-hydroxypentyl acrylate, 2,2-dimethyl-3-hydroxypropyl acrylate, 2-methoxyethyl acrylate, 3-methoxybutyl acrylate, 2-ethoxyethyl acrylate, 2-iso-propoxyethyl acrylate, 2-butoxyethyl acrylate, 2-(2-methoxyethoxy)ethyl acrylate, 2-(2-butoxyethoxy)ethyl acrylate, 1-bromo-2-methoxyethyl acrylate, 1,1-dichloro-2-ethoxyethyl acrylate, methyl methacrylate, ethyl methacrylate, hydroxyethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, sec-butyl methacrylate, amyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, benzylmethacrylate, chlorobenzyl methacrylate, octyl methacrylate, N-ethyl-N-phenylaminoethyl methacrylate, 2-(3-phenylpropyloxy)ethyl methacrylate, dimethylaminophenoxyethyl methacrylate and furfuryl methacrylate. Aromatic examples include but are not limited to 4-alkyl phenylacrylate or methacrylate, phenyl methacrylate, phenyl acrylate, and  $\beta$ -naphthyl methacrylate.

35 Preferred optionally substituted styrenes include styrene, methylstyrene, dimethylstyrene, trimethylstyrene, ethylstyrene, diethylstyrene, isopropylstyrene, butylstyrene, hexylstyrene, cyclohexylstyrene, decylstyrene, chloromethylstyrene, trifluoromethylstyrene, ethoxymethylstyrene, acetoxymethylstyrene, methoxystyrene, 4-methoxy-3-methylstyrene, dimethoxystyrene, chlorostyrene, dichlorostyrene,



trichlorostyrene, tetrachlorostyrene, pentachlorostyrene, bromostyrene, dibromostyrene, iodostyrene, trifluorostyrene and 2-bromo-4-trifluoromethylstyrene.

Preferred methacrylamides contain less than 12 carbon atoms. Examples include methylmethacrylamide, tert-butylmethacrylamide, tert-octylmethacrylamide, benzylmethacrylamide, cyclohexylmethacrylamide, phenylmethacrylamide, dimethylmethacrylamide, dipropylmethacrylamide, hydroxyethyl-N-methylmethacrylamide, N-methylphenylmethacrylamide, N-ethyl-N-phenylmethacrylamide and methacrylhydrazine.

Preferred allyl compounds include allyl acetate, allyl caprylate, allyl caprylate, allyl laurate, allyl palmitate, allyl stearate, allyl benzoate, allyl acetoacetate, allyl lactate, allyloxyethanol, allyl butyl ether and allyl phenyl ether.

The hydrophilic acrylic polymer may be prepared in a conventional manner by polymerising the olefinically unsaturated monomers having ionic and/or non-ionic water-dispersing groups, optionally in the presence of olefinically unsaturated monomers which are free from ionic and non-ionic water-dispersing groups. Temperatures from 20°C to 180°C are preferred. The polymerisation may be continued until reaction between the monomers is complete or the desired Mn has been reached.

Preferred polymerisation methods include solution polymerisation, emulsion polymerisation, suspension polymerisation and solution/dispersion polymerisation and such general methods as are well known in the art.

If desired, an initiator may be used to assist acrylic polymer formation. Suitable initiators include free-radical generators. Examples of initiators include azobis compounds, peroxides, hydroperoxides, redox catalysts, potassium persulfate, ammonium persulfate, tert-butyl peroctoate, benzoyl peroxide, isopropyl percarbonate, 2,4-dichlorobenzoyl peroxide, methyl ethyl ketone peroxide, cumene hydroperoxide, dicumyl peroxide, azobisisobutyronitrile, azobis(2-amidino-propane)hydrochloride and the like. Typically 0.05 to 5% by weight of initiator is used relative to the total weight of the monomers. Preferably the polymerisation is performed in the presence of an emulsifying agent.

Optionally the hydrophilic acrylic polymer is prepared by a process in which the Mn is controlled by the addition of chain transfer agents and/or through the adjustment of the ratio of the concentration of monomers relative to the concentration of initiator during the course of the polymerisation. Typical chain transfer agents are thiols, halocarbons and cobalt macrocycles.

When component (a) is a hydrophilic polyurethane the Mn is preferably less than 12,500, more preferably less than 10,000 especially less than 7,500 and more especially less than 5,000. Preferred hydrophilic polyurethanes are linear.

The hydrophilic polyurethane is preferably obtained from the reaction of at least one organic polyisocyanate and at least one isocyanate-reactive compound having ionic

and/or non-ionic water-dispersing groups, optionally in the presence of isocyanate-reactive compounds which are free from ionic and non-ionic water-dispersing groups.

The organic polyisocyanate may be any known in the art, preferably having two isocyanate groups, and may for example be an aliphatic, cycloaliphatic, aromatic or araliphatic isocyanate. Examples of suitable organic polyisocyanates include ethylene diisocyanate, 1,6-hexamethylene diisocyanate, isophorone diisocyanate, tetramethylxylene diisocyanate, 1,4-phenylene diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 4,4'-diphenyl-methane diisocyanate and its hydrogenated derivative, 2,4'-diphenylmethane diisocyanate and its hydrogenated derivative, and 1,5-naphthylene diisocyanate. Mixtures of the polyisocyanates can be used, particularly isomeric mixtures of the toluene diisocyanates or isomeric mixtures of the diphenylmethane diisocyanates (or their hydrogenated derivatives), and also organic polyisocyanates which have been modified by the introduction of urethane, allophanate, urea, biuret, carbodiimide, uretonimine or isocyanurate residues.

Preferred organic polyisocyanates include cycloaliphatic polyisocyanates, especially isophorone diisocyanate, and aliphatic isocyanates, especially 1,6-hexamethylene diisocyanate or hydrogenated 4,4-diphenyl methyl diisocyanate.

The isocyanate-reactive compound preferably has at least one, more preferably two isocyanate-reactive groups. Optionally isocyanate-reactive compounds having three isocyanate-reactive groups may be present, preferably in low levels not exceeding 5% by weight relative to the total weight of the isocyanate-reactive compound. Preferred isocyanate-reactive groups are selected from -OH, -NH<sub>2</sub>, -NH- and -SH. These isocyanate-reactive groups are capable of reacting with an isocyanate (-NCO) group.

Preferred isocyanate-reactive compounds having water-dispersing groups include low molecular weight polyols or polyamines bearing ionic and/or non-ionic water-dispersing groups. Preferred isocyanate-reactive compounds having anionic water-dispersing groups are diols having one or more sulphonic acid groups and/or carboxylic acid groups, more preferably dihydroxy alkanolic acids, especially 2,2-dimethylol propionic acid. Preferred isocyanate-reactive compounds having non-ionic water-dispersing groups are diols providing polyethyleneoxide and/or polypropyleneoxide groups.

Preferred isocyanate-reactive compounds which are free from ionic and non-ionic water-dispersing groups include organic polyol(s) and / or polyamine(s). Preferred organic polyols or polyamines have a Mn up to 3000, more preferably up to 2000, especially from 400 to 2000. Preferred organic polyols are diols. The diols include members of any of the chemical classes of diols used or proposed to be used in polyurethane formulations. In particular, the diols are preferably polyesters, polyesteramides, polyethers (other than ones providing polyethyleneoxide and/or polypropyleneoxide groups), polythioethers, polycarbonates, polyacetals, polyolefins or polysiloxanes. Further examples of optional diols which are free from ionic and non-ionic water-dispersing groups include organic diols

having an Mn below 400. Examples of such diols include ethylene glycol, diethylene glycol, tetraethylene glycol, bis(hydroxyethyl) terephthalate, cyclohexane dimethanol, and furan dimethanol.

The hydrophilic polyurethane may be prepared in a conventional manner by reacting the components having isocyanate groups with the components having isocyanate-reactive groups. Substantially anhydrous conditions are preferred. Temperatures of from 30°C and 130°C are preferred and the reaction is preferably continued until the reaction between the isocyanate groups and the isocyanate-reactive groups is substantially complete.

The relative amounts of the organic polyisocyanate and the isocyanate-reactive compounds are preferably selected such that the mole ratio of isocyanate groups to isocyanate-reactive groups is about 2:1 to 1:2, preferably from about 1.4:1 to 1:1.4. Alternatively an isocyanate-group terminated polyurethane prepolymer may be prepared in a two stage process either in solvent or as a melt, wherein the ratio of isocyanate groups to isocyanate-reactive groups is from about 1.1:1 to 2:1, preferably from about 1.1:1 to 1.9:1.

Terminating compounds, for example compounds having one isocyanate group or one isocyanate-reactive group, may be used to cap-off any excess isocyanate or isocyanate-reactive end groups in the polyurethane resulting from the reaction of the organic polyisocyanate and isocyanate-reactive compound. Compounds having one isocyanate-reactive group include, for example, monoalcohols, monoamines and monothiols, especially isopropanol. Compounds having one isocyanate reactive groups include alkyl monoisocyanates. The Mn of the polyurethane may be controlled through the use of terminating compounds. The terminating compounds may also bear ionic and/or non-ionic water-dispersing groups, for example those hereinbefore described.

If desired a catalyst may be used to assist polyurethane formation. Suitable catalysts include di-butyl tin dilaurate, stannous octoate and tertiary amines as known in the art.

Preferably the hydrophilic polyurethane is not prepared by chain-extension of an isocyanate-terminated polyurethane prepolymer (for example by mixing the hydrophilic polyurethane with water or water mixed with chain extenders).

When component (a) is a hydrophilic polyester polymer, the Mn is preferably in the range from 500 to 30,000, more preferably in the range from 1000 to 25,000.

The Tg of the hydrophilic polyester is preferably in the range -38°C to 105°C.

The hydrophilic polyester is preferably obtained by polymerising at least one monomer having two or more functional groups which will readily undergo an ester condensation reaction and having ionic and/or non-ionic water-dispersing groups, optionally in the presence of monomers having two or more functional groups which will readily undergo an ester condensation reaction which are free from ionic and non-ionic

water-dispersing groups. Preferred anionic water-dispersing groups are as mentioned above, especially sulphonic acid groups, ionised sulphonate groups and carboxylic acid groups and ionised carboxyl groups.

Functional groups which will readily undergo an ester condensation reaction include carboxyl groups, hydroxyl groups and esterifiable derivatives thereof. Examples of such monomers are aromatic dicarboxylic acids having an ionised sulphonate group. Particularly preferred is sodio-5-sulpholsophthalic acid (SSIPA).

Other useful monomers which have two or more groups which readily undergo an ester condensation reaction and have one or more sulphonate groups are dihydroxy aryl monomers having at least one sulphonate group.

The amount of ionised sulphonate and/or carboxy and/or non-ionic water-dispersing groups present in the hydrophilic polyester is preferably sufficient to provide water-dissipatability of the polyester. Ionised sulphonate groups are more effective at providing or contributing to water-dissipatability than ionised carboxy groups and so can be used at considerably lower levels in comparison to ionised carboxy groups.

When the hydrophilic polyester mainly contains SSIPA as the monomer for providing the ionised sulphonate groups, the amount of this monomer used in the polyester synthesis, based on the weight of all the monomers used in the polyester synthesis, will usually be within the range from 5 to 20% by weight. The carboxylic acid value of the hydrophilic polyester which contains mainly ionised sulphonate groups will generally be within the range of from 0 to 100 mgKOH/g, more preferably 0 to 50 mgKOH/g, especially 0 to 25 mgKOH/g, more especially 0 to 10mgKOH/g.

When the hydrophilic polyester predominantly contains ionised carboxy water-dispersing groups, the carboxylic acid value of the polyester is preferably within the range of from 20 to 140 mgKOH/g more preferably 30 to 100 mgKOH/g.

Monomers having two or more functional groups which will readily undergo an ester condensation reaction and having non-ionic water-dispersing groups include polyethylene oxide chains, ethylene oxide-containing mono, di or higher functional hydroxy compounds, especially polyethylene glycols and alkyl ethers of polyethylene glycols. A small segment of a polyethylene oxide chain can be replaced by a propylene oxide or butylene oxide chain in such non-ionic groups, but should still contain ethylene oxide as a major part of the chain.

When the hydrophilic polyester contains polyethylene oxide chains, the polyethylene oxide chain content preferably does not exceed 25% by weight, more preferably does not exceed 15% by weight, based on the total weight of the polyester.

Monomers having two or more functional groups which will readily undergo an ester condensation reaction and are free from ionic and non-ionic water-dispersing groups include polybasic carboxylic acids and polyols where the carboxylic acid groups and

hydroxy groups are esterified during the polymerisation process. For example, aliphatic, alicyclic and aromatic compounds having two or more carboxy groups and their ester forming derivatives (e.g. esters, anhydrides and acid chlorides) may be used. Specific examples include adipic acid, fumaric acid, maleic acid, succinic acid, itaconic acid, sebacic acid, nonanedioic acid, decanedioic acid, 1,4-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,2-cyclohexanedicarboxylic acid, terephthalic acid, isophthalic acid, phthalic acid and tetrahydrophthalic acid and their acid chlorides. Anhydrides include succinic, maleic, phthalic and hexahydrophthalic anhydrides.

Preferred polyols which can be used to form the polyester include those having from 2 to 6, more preferably 2 to 4 and especially 2 hydroxyl groups per molecule. Suitable polyols having two hydroxy groups per molecule include diols such as 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, 2,2-dimethyl-1,3-propanediol (neopentyl glycol), the 1,2-, 1,3- and 1,4-cyclohexanediols and the corresponding cyclohexane dimethanols, diethylene glycol, dipropylene glycol, and diols such as alkoxyated bisphenol A products, e.g. ethoxyated or propoxyated bisphenol A. Suitable polyols having three hydroxy groups per molecule include triols such as trimethylolpropane (1,1,1-tris (hydroxymethyl)ethane). Suitable polyols having four or more hydroxy groups per molecule include pentaerythritol (2,2-bis(hydroxymethyl)-1,3-propanediol) and sorbitol (1,2,3,4,5,6-hexahydroxyhexane).

The hydrophilic polyester is optionally dissipated in water by adding the solidified melt directly into water. Alternatively, water can be added directly to the hot polyester melt until the desired solids content/viscosity is reached. Still further, the hydrophilic polyester can be dissipated in water by adding an aqueous pre-dissipation (or organic solvent solution) of the polyester to the water phase.

Preferably Component (b) readily disperses in Component (d). On dispersion the particle size of component (b) is preferably such that when present in the composition it has a particle size from 20 to 500nm, more preferably from 20 to 350nm, especially from 20 to 200nm. Particle size can be measured by, for example, laser light scattering electron microscopy.

Component (b) is preferably an hydrophobic acrylic or polyurethane polymer of Mn greater than 40,000. The hydrophobic polymer is preferably prepared by the methods described above for the hydrophilic polymers, except that the ionic and non-ionic water-dispersing groups are omitted or are present in low amounts.

When component (b) is a hydrophobic acrylic polymer the preferred acid value is from 0 to 30 mgKOH/g.

The Tg of the hydrophobic acrylic polymer is preferably greater than -10°C, more preferably greater than 120°C.

Preferably the hydrophobic acrylic polymer is a copolymer comprising styrene.

When component (b) is a hydrophobic polyurethane polymer, the hydrophobic polyurethane polymer can optionally be prepared by chain extending an isocyanate terminated polyurethane prepolymer, using techniques well known in the art. Suitable chain extenders include polyols, amine alcohols, diamines, hydrazines, substituted hydrazines and water. When the chain extender is other than water, for example a diamine, it may be added to an aqueous dispersion of the polyurethane prepolymer or may already be present in the aqueous medium when the polyurethane prepolymer is dispersed therein. The hydrophobic polyurethane polymer may be linear, branched or crosslinked.

Component (a) and component (b) are optionally based on the same or different polymers. For example component (a) may be a hydrophilic polyurethane and component (b) a hydrophobic polyurethane or component (a) may be a hydrophilic polyurethane and component (b) may be a hydrophobic acrylic polymer, in each case having the Mn as specified above.

Components (a) and (b) optionally each comprise a mixture of polymers. For example component (a) may comprise a mixture of hydrophilic acrylic polymers or a mixture of a hydrophilic acrylic polymer and a hydrophilic polyurethane polymer.

Components (a) and (b) are purified if desired in the usual way for colorants used in ink jet printing inks, for example by ion-exchange, filtration, reverse osmosis, dialysis, ultra-filtration or a combination thereof. In this way one may remove co-solvents used for the polymerisation, low molecular weight salts, impurities and free monomers.

Components (a) and (b) can be combined in a number of ways. For example, components (a) and (b) can be prepared separately, followed by combination by simple blending. Alternatively, component (b) can be prepared by aqueous polymerisation in the presence of component (a), or component (a) can be prepared by *in-situ* polymerisation in component (b) prepared by emulsion polymerisation.

For example when component (b) is a hydrophobic acrylic polymer, the hydrophobic acrylic polymer may be prepared by aqueous polymerisation, using component (a) (hydrophilic acrylic, polyurethane and/or polyester polymer) as a polymeric dispersant. Optionally additional surfactant may be used to aid dispersion. Preferably the aqueous polymerisation is carried out at a pH above 7.

Alternatively when component (b) is a hydrophobic acrylic polymer the polymer may be prepared by emulsion polymerisation at a low pH followed by *in-situ* polymerisation of a hydrophilic acrylic polymer component (a) at a low pH, with subsequent neutralisation with a base to pH 7.

The weight ratio of component (a) to component (b) is preferably from 5:95 to 50:50, more preferably from 5:95 to 40:60, especially of from 10:90 to 40:60.

The pigment (component (c)) is preferably a water-insoluble colorant, preferably inorganic or organic. Preferred inorganic pigments include carbon black, titanium dioxide, zinc oxide, zirconium oxide, chromium oxide, iron oxide and combinations thereof.

Preferred organic pigments include phthalocyanine, anthraquinone, perinone, indigold, perylene, azo, carbon black pigments carrying ionic groups, azomethine, condensed ring pigments and pigments as mentioned in the Colour Index International, Third Edition (1982) Pigments and Solvent dyes, pages 10 to 143, which are incorporated herein by reference thereto. Preferred organic pigments are yellows, reds, oranges, violets, blue and / or black.

The carbon black pigment optionally carries ionic groups, for example anionic and/or cationic groups. The anionic group preferably comprises a carboxylic, sulphonic or phosphonic acid group. The cationic group preferably comprises a quaternary ammonium group. Carbon black pigments carrying ionic groups are commercially available from a number of sources, including Mitsubishi and Cabot corporation for example the Cabotjet range of carbon black pigments. Particularly preferred is carbon black pigment having a mean particle size of from 5 to 100 nm, more preferably of from 10 to 30 nm. The carbon black pigment preferably has a pH of from 3 to 9.

The pigment used in the composition of the present invention is optionally mixture comprising of two or more pigments. Pigments are present in any effective amount in the composition, typically from about 1 to about 10 percent by weight of the composition.

The liquid medium (component (d)) preferably comprises water and an organic solvent. The organic solvent preferably comprises a water-miscible organic solvent and/or a water-immiscible organic solvent.

Suitable water-miscible organic solvents include methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, isobutanol, dimethylformamide, dimethylacetamide, acetone, diacetone alcohol, tetrahydrofuran, dioxane, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol, diethylene glycol, thiodiglycol, polyethylene glycol, polypropylene glycol, glycerol, 1,2,6-hexanetriol, 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy) ethanol, 2-(2-butoxyethoxy)ethanol, 3-butoxypropan-1-ol, 2-[2-(2-methoxyethoxy)-ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)ethoxy]-ethanol, optionally substituted pyrrolidones, sulpholane and mixtures containing two or more of the aforementioned water-miscible organic solvents. Preferred water-miscible organic solvents are tetrahydrofuran, dioxane, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol, optionally substituted pyrrolidones, and sulpholane.

Suitable water-immiscible organic solvents include toluene, xylene, naphthalene, tetrahydronaphthalene, methyl naphthalene, chlorobenzene, fluorobenzene, chloronaphthalene, bromonaphthalene, butyl acetate, ethyl acetate, methyl benzoate, ethyl benzoate, benzyl benzoate, butyl benzoate, phenylethyl acetate, butyl lactate,

benzyl lactate, diethyleneglycol dipropionate, dimethyl phthalate, diethyl phthalate, dibutyl phthalate, di (2-ethylhexyl) phthalate, hexanol, octanol, benzyl alcohol, phenyl ethanol, phenoxy ethanol, phenoxy propanol, phenoxy butanol, anisole, phenetole, nitrocellulose, cellulose ether, cellulose acetate, low odour petroleum distillates, turpentine, white spirits, naphtha, isopropylbiphenyl, terpene, vegetable oil, mineral oil, essential oil, natural oil, C<sub>6</sub>-C<sub>12</sub> substituted pyrrolidones and mixtures of any two or more thereof. Benzyl alcohol is especially preferred.

The weight ratio of water-miscible organic solvent to water-immiscible organic solvent in the composition is preferably 19:1 to 1:1, more preferably 8:1 to 1:1, especially 5:1 to 1:1.

The compositions according to the present invention may be prepared by combining components (a), (b), (c) and (d). Suitable techniques are well known in the art, for example agitation, grinding, milling, ultrasonication or stirring of all the components. Preferably the composition is prepared by mixing components (a), (b), and (d) and optionally further components until the composition is homogenous. The mixture may then be added slowly with stirring to component (c) before adjusting the pH by addition of a base. Components (a), (b), (c) and (d) are preferably combined together under conditions which retain stability and avoid flocculation. The preferred pH range of the composition is of from 7 to 11, more preferably of from 9 to 10.

Preferably the composition comprises:

(i) from 0.1 to 10 parts, more preferably 1 to 5 parts, especially 2 to 4 parts of component (a);

(ii) from 1 to 10 parts, more preferably 2 to 9 parts, especially 4 to 7 parts of component (b);

(iii) from 0.1 to 15 parts, more preferably 2 to 10 parts, especially 4 to 8 parts of component (c); and

(iv) from 75 to 98 parts, more preferably 75 to 90 parts, especially 80 to 90 parts of component (d);

wherein all the parts are by weight and the parts by weight of (i) + (ii) + (iii) + (iv) add up to 100.

The composition optionally contains a biocide, for example Proxel GXL (Proxel is a trade mark of Zeneca Limited) or Kathon (Kathon is a trade mark of Rohm and Haas), a fungicide, a rheological agent, e.g. a wax (e.g. beeswax), a clay (e.g. bentonite), an IR absorber, or a fluorescent brightener, for example C.I. Fluorescent Brightener 179 and/or UV absorber, for example hydroxy phenylbenzotriazole. Furthermore the compositions optionally contain a surface active agent, wetting agent and/or an emulsifier, for example those described in McCutcheon's Emulsifiers and Detergents 1996 International Edition or in Surfactants Europa 3<sup>rd</sup> Edition 1996 each of which is incorporated herein by reference.



Preferably the composition is an ink, more preferably an ink suitable for use in an ink jet printer.

The viscosity of the composition is preferably less than 100cp, more preferably less than 50cp, especially less than 20cp and more especially less than 15cp, at 20°C.

Preferably the composition has been filtered through a filter having a mean pore size below 10  $\mu\text{m}$ , preferably below 5  $\mu\text{m}$ , more preferably below 2  $\mu\text{m}$ , especially below 0.45  $\mu\text{m}$ . In this way particulate matter is removed which could otherwise block fine nozzles in an ink-jet printer.

The compositions according to the invention have the advantage that they are suitable not only for the use in piezoelectric ink jet printers but also in thermal and continuous ink jet printers. Such compositions form discrete droplets on the substrate with little tendency for diffusing. Consequently sharp images with excellent print quality and little if any bleed between colours printed side by side can be obtained. Furthermore the compositions show good storage stability, wet and light fastness and fastness to both acidic and alkaline highlighter pens.

A third aspect of the invention provides a process for printing an image on a substrate comprising applying thereto a composition according to the invention by means of an ink jet printer.

The ink jet printer preferably applies the composition to the substrate in the form of droplets which are ejected through a small nozzle onto the substrate. Preferred ink jet printers are piezoelectric ink jet printers and thermal ink jet printers. In thermal ink jet printers, programmed pulses of heat are applied to the compositions in a reservoir by means of a resistor adjacent to the nozzle, thereby causing the compositions to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the nozzle. In piezoelectric ink jet printers the oscillation of a small crystal causes ejection of the compositions from the nozzle.

The substrate is preferably a paper, plastic, or textile material, more preferably a paper, an overhead projector slide or a textile material, especially paper.

Preferred papers are plain, coated or treated papers which may have an acid, alkaline or neutral character. Most preferably the substrate is a coated paper.

According to a further feature of the invention there is provided an ink jet printer cartridge, optionally refillable, containing a composition as hereinbefore defined.

The invention will now be described by example only. All parts and percentages are by weight unless specified otherwise.

Example 1 - Preparation of components (a) and (b) by emulsion polymerisation. Component (a) is a hydrophilic acrylic copolymer and component (b) is a hydrophobic acrylic polymer (polystyrene) and the ratio of component (a) to component (b) is 35:65.

Stage 1 Preparation of a hydrophilic acrylic copolymer of Mn less than 30,000  
MAA/MMA/BA (10/69.5/20.5).

Table 1

5

	Materials	Weight (g)	Percentage
	De-ionised Water	436.5	32.82
<u>monomer shot</u>	Methyl methacrylate	25.9	1.9
	Butyl acrylate	7.6	0.6
	3 Mercaptopropionic acid	1.1	0.08
<u>monomer feed</u>	Methacrylic acid (MAA)	37.4	2.8
	Methyl methacrylate (MMA)	233.7	17.6
	Butyl acrylate (BA)	68.8	5.2
	3-Mercaptopropionic acid	10.0	0.7
<u>initiator shot</u>	Ammonium persulphate	0.4	0.03
	De-ionised water	12.0	0.9
	Sodium lauryl sulphate	0.6	0.04
<u>initiator feed</u>	Ammonium persulphate	3.3	0.25
	De-ionised water	108.5	8.16
	Sodium lauryl sulphate	5.0	0.4
<u>burn-up</u>	Ascorbic acid	2.243	0.17
<u>co-Initiator</u>	De-ionised water	42.58	3.20
<u>burn-up</u>	t-Butyl hydrogen peroxide (70% solids)	3.20	0.24
<u>initiator</u>	De-ionised water	41.62	3.13
<u>odour reducer</u>	Hydrogen peroxide solution (30% solids)	2.49	0.19
	De-ionised water to take up to 30% solids	2.50	18.50
<u>neutralisation</u>	Ammonia solution 20%	36.91	2.78

Water was added to a reactor and heated to 80°C with continuous stirring. The reactor was purged with N<sub>2</sub>.

The monomer shot was added to the reactor and stirred for 5 minutes. The initiator shot was added to seed the reaction and stirred for 15 minutes. Monomer and initiator feeds were then added over 90 minutes whilst maintaining the temperature at 80-83°C for a further hour.

Subsequently the emulsion was cooled to 50°C to commence burn-up by adding the burn-up co-initiator dropwise over 30 minutes. The burn-up initiator was added in 3 equal shots at 1, 10 and 20 minutes of the burn-up co-initiator addition.

The mixture was stirred for 30 minutes before adding the hydrogen peroxide solution dropwise over 10 minutes. De-ionised water was added to take the emulsion to 30% solids w/w and the temperature increased to 60°C.

The emulsion was then neutralised with ammonia solution and stirred until the solution had gone clear. The resultant hydrophilic polymer was cooled and filtered through a 50µm mesh.

#### Analysis

The resultant hydrophilic polymer solution (component (a)) had a pH of 7.0, a weight average molecular weight of 13289 and an Mn of 5,446. The Tg average was 66°C.

Stage 2 - Preparation of a mixture comprising a hydrophilic polymer of Mn less than 30,000 and a hydrophobic polymer of Mn greater than 40,000

Preparation of component (b) (polystyrene) by emulsion polymerisation in the presence of component (a) prepared in stage 1, with components as listed in Table 2.

Table 2

	Materials	Weight (g)	Percentage
<u>initial charge</u>	Product from stage 1.	386.68	34.40
	De-ionised water	379.77	33.79
	Ammonia solution 35%	10.0	0.89
<u>emulsified feed</u>	Styrene	217.74	19.37
	De-ionised water	108.88	9.69
	Ammonium persulphate	1.09	0.1
	Sodium lauryl sulphate	1.09	0.1
	De-ionised water for rinse	18.75	1.69

The initial charge was added to a reactor with enough ammonia solution to ensure that the pH of the initial charge was greater than 8.5, and heated to 80-85°C with continuous stirring under nitrogen.

10% of the emulsified feed was added to the reactor from a dropping funnel and left to nucleate for about 5 minutes. After nucleation the remainder of the emulsified feed was added over an hour while the temperature of  $85 \pm 2^\circ\text{C}$  was maintained. Once all the feed was added the dropping funnel was rinsed with de-ionised water which was subsequently added to the reactor. The reaction was left for a further 30 minutes at 85°C before cooling the resultant composition to room temperature and filtering the composition through a 50µm mesh.

The pH of the composition was 8.8, the particle size was 38 nm and the Mn of component (b) was 214,000.

The resultant composition comprised a hydrophilic polymer of Mn less than 30,000 and a hydrophobic polymer of Mn greater than 40,000, in a weight ratio of approximately 35:65. More especially the composition comprised the components listed in Table 3

Table 3

Component in Solid Resin	Percentage
MAA	3.25
MMA	22.62
BA	6.66
3 mercaptopropionic acid	0.96
Styrene	64.58
Ammonium persulphate	0.65
Sodium lauryl sulphate	0.81
Ascorbic acid	0.20
t-Butyl hydrogen peroxide	0.20
Hydrogen peroxide	0.07

Example 2 Preparation of a blend comprising a hydrophilic polymer of Mn less than 30,000 and a hydrophobic polymer of Mn greater than 40,000.

Component (a) is an acrylic copolymer and component (b) is an acrylic copolymer prepared via emulsion polymerisation.

Stage 1 - Preparation of a hydrophilic acrylic copolymer of Mn less than 30,000  
MAA/MMA (10/90)

Example 1, stage 1 was repeated except that the monomer shot and monomer feed were as described in Table 4.

5

Table 4

		<u>weight (g)</u>
<u>monomer shot</u>	methyl methacrylate	33.7
	3-mercaptopropionic acid	1.1
<u>monomer feed</u>	methacrylic acid	37.4
	methyl methacrylate	302.9
	3-mercaptopropionic acid	10.0

Analysis

10

The resultant hydrophilic polymer solution had a solids content of 30%w/w, a pH of 7.0 and a Mn of 5541.

Stage - 2 Preparation of a hydrophobic polymer of Mn greater than 40,000

15

Preparation of component (b) a styrene/acrylic acid (96/4) copolymer by emulsion polymerisation, with components as listed in Table 5.

Table 5

	Materials	Weight (g)	Percentage
<u>monomer shot</u>	De-ionised water	442.2	33.95
	Styrene	48	3.7
	Acrylic acid	2	0.15
<u>monomer feed</u>	Styrene	432	33.2
	Acrylic acid	18	1.4
<u>initiator shot</u>	Ammonium persulphate	0.25	0.02
	Sodium lauryl sulphate	1.0	0.08
	De-ionised water	13.1	1.0
<u>initiator feed</u>	Ammonium persulphate	2.25	0.17
	Sodium lauryl sulphate	9.0	0.7
	De-ionised water	117.8	9.0
<u>burn-up co-initiator</u>	Ascorbic acid		
	De-ionised water	1.5	0.12
		28.5	2.19
<u>burn-up initiator</u>	t-Butyl hydrogen peroxide		
	De-ionised water	2.14	0.16
		27.86	2.14
<u>neutralisation</u>	De-ionised water		
	Ammonia solution 35%	143.37	11.01
		13.5	1.04

5 Water was added to a reactor and heated to 80°C with continuous stirring. The reactor was purged with N<sub>2</sub>.

The monomer shot was added to the reactor and stirred for 5 minutes. The initiator shot was added to seed the reaction and stirred for 15 minutes. Monomer and initiator feeds were then added over 90 minutes whilst maintaining the temperature at 80-83°C for a further hour.

Subsequently the emulsion was cooled to 50°C to commence burn-up by adding the burn-up co-initiator dropwise over 30 minutes. The burn-up Initiator was added in 3 equal shots at 1, 10 and 20 minutes of the burn-up co-initiator addition.

5 The mixture was stirred for 30 minutes before adding the hydrogen peroxide before adding the hydrogen peroxide solution dropwise over 10 minutes. De-ionised water was added to take the emulsion to 30% solids w/w and the temperature increased to 60°C.

10 The emulsion was then neutralised with ammonia solution and stirred until the mixture had gone clear. The resultant hydrophobic polymer was cooled and filtered through a 50µm mesh.

#### Analysis

The resultant hydrophobic polymer had a pH of 9.6, an average particle size of 94 nm, and Mn of 80,195.

#### Stage 3 - Preparation of a blend of Components (a) and (b)

15 Component (a) from stage 1 (28g) was added to component (b) from stage 2 (39g) in de-ionised water (13g) and mixed thoroughly to give a final blend having a solids content of 30%.

#### Example 3

#### Aqueous Pigment Inks

#### Stage 1 - Preparation of Ink Composition

20 Diethylene glycol, urea, butyl digol, surfynol 465, water and the combination of the hydrophilic and hydrophobic polymers resulting from example 1 and example 2 respectively were mixed until homogenous. This mixture was added slowly with stirring to Cabojet 300 millbase.

25 The resultant composition was adjusted to approximately pH 9.5 using 35% ammonia solution, and subsequently filtered through a 10µm mesh.

The resulting ink compositions were as follows:

30

<u>Ink Compositions</u>	<u>weight%</u>
Cabojet 300 @ 15.3w/w % solids in water	26
Diethylene glycol	10
Urea	5
35 Butyl Digol	2
Surfynol 465	0.1
Product from example 1 and example 2	
respectively @ 30% w/w % solids in water	33.3
De-ionised water	23.6

Stage 2 - EvaluationEvaluation

The inks resulting from Stage 1 were fired from an Epson 600 thermal ink-jet printer onto Conqueror High White Wove 100g/m<sup>2</sup> plain paper from Arjo Wiggins Ltd.

Controls are a polymer free formulation, a formulation with only component (a) and a formulation with only component (b). Prints were evaluated for highlighter smear and wet rubfastness. Inks were evaluated for stability. The evaluation test results are shown in Table 6.

Highlighter smear

This is a test performed 5 minutes after printing.

A yellow highlighter pen was used to draw a horizontal line across a series of printed vertical bars. The amount of ink smear between the vertical bars was assessed visually against controls.

Wet rubfastness

This is a test performed 5 minutes after printing.

A finger was wetted and rubbed on the corner of a printed solid black block. The amount of ink transferred to white paper is assessed visually against controls.

Ink Stability

The ink resulting from stage 1 were stored in an incubator at a range of temperatures for one week. The temperature cycle was a 24 hour cycle (-10°C to 25°C).

The stability was evaluated by optical microscopy and the stability was ranked as follows:

Rank	Description
5	No change, good mobile dispersion
4	Good, a few 1 micron particles present, still mobile
3	An increase in the amount of particles greater than 1 micron
2	Large (greater than 2 micron) flocculates present, ink less mobile
1	Flocculated, immobile, unstable



Table 8 Evaluation Test Results

Example	Polymer	Ink Stability data				Printed Ink Performance	
		Room temperature	60°C	70°C	Temperature cycle	wet rub fastness	highlighter smear
Control	No polymers	5	5	5	5	smear	smear
Example 2	Component (a) only	1	1	1	1	did not print	did not print
Example 2	Component (b) only	5	5	5	5	did not print	did not print
Example 1	Insitu component (a) + component (b)	5	5	2	5	v. little smear	no smear 100%
Example 2	Blend of component (a) + component (b)	5	5	5	5	v. little smear	no smear 100%

CLAIMS

1. A composition comprising the components:

- 5           (a)     a hydrophilic polymer having a number average molecular weight less than 30,000;  
          (b)     a hydrophobic polymer having a number average molecular weight more than 40,000;  
          (c)     pigment; and  
10          (d)     liquid medium.

2.     A composition according to claim 1 wherein component (a) has a number average molecular weight less than 20,000.

15     3.     A composition according to claim 1 wherein component (b) has a number average molecular weight greater than 60,000.

4.     A composition according to claim 1 wherein component (a) and component (b) are each independently selected from the group consisting of acrylic polymers, polyurethanes  
20       and polyesters.

5.     A composition according to any one of the preceding claims wherein the hydrophobic polymer comprises a hydrophobic acrylic polymer and a polyurethane polymer.  
25

6.     An composition according to any one of the preceding claims wherein the hydrophilic polymer is hydrophilic by virtue of the presence of ionic and/or non-ionic water dispersing groups in the hydrophilic polymer.

30     7.     A composition according to any one of the preceding claims having a viscosity less than 100cp at 20 °C.

8.     A composition according to any one of the preceding claims which comprises:

- 35       (i) from 0.1 to 10 parts of component (a);  
       (ii) from 1 to 10 parts of component (b);  
       (iii) from 0.1 to 15 parts of component (c); and  
       (iv) from 75 to 98 parts of component (d)  
       wherein all the parts are by weight and the parts by weight of (i) + (ii) + (iii) + (iv) add up to 100.

9. A composition according to anyone of the preceding claims wherein the pigment is a carbon black pigment.

5 10. A composition according to claim 9 wherein the carbon black pigment carries ionic groups.

11. An ink comprising a composition according to any one of the preceding claims.

10 12. Use of a composition according to claims 1 to 10 as an ink for ink-jet printing.

13. A process for printing an image on a substrate comprising applying thereto composition according to any one of claims 1 to 10 by means of an ink jet printer.

15 12. An ink jet printer cartridge containing a composition according to any one of claims 1 to 10.

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Avecia Ltd